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PATENT SPECIFICATION

NO DRAWINGS

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Inventor: JOHN DAVID SEDDON

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Int. Cl.:—C 08 f 1/58

COMPLETE SPECIFICATION

Polymerisation process using Metal Carbonyl Catalysts

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polymerisation processes and more particularly to processes for polymerising ethylinically unsaturated monomers.

It has always been assumed that reactions involving metal carbonyls must be effected in the substantial absence of atmospheric oxygen. We have found that free radical initiated polymerisation processes using metal carbonyl initiators may be effected without the need for taking precautions to exclude atmospheric oxygen.

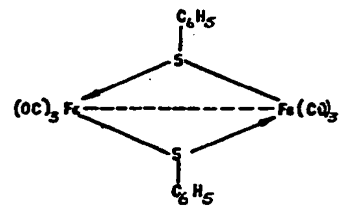
According to the present invention we provide a process for polymerising ethylenically unsaturated material normally polymerisable by a free radical mechanism which comprises contacting the material with a transition metal carbonyl in the presence of a halogenated organic compound and in the presence of more than 100 parts per million by volume of atmospheric oxygen.

By the process of our invention, the polymerisation of the ethylenically unsaturated material proceeds satisfactorily without any precautions whatsoever being taken to remove atmospheric oxygen although we do not exclude the possibility of some oxygen being removed if desired. However, it is to be understood that the polymerisation of ethylenically unsaturated material by contact with a metal carbonyl in the presence of an organic halide, using the processes operated hitherto wherein great care is taken to reduce the oxygen present to a very small concentration (i.e. less than 100 parts per million by volume) forms no part of our invention.

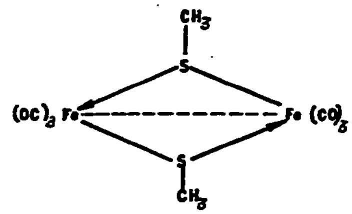
The ethylenically unsaturated monomers suitable for polymerisation according to the process of our invention are those whose polymerisation is normally initiated by free radical catalysts and especially those containing an electron-attracting group, e.g. a carboxylic acid or ester group, attached to an ethylenically bound carbon atom. Examples of monomers containing electron-attracting groups include acrylic acid, a substituted acrylic acid or functional derivatives thereof (for example acrylic and methacrylic acids, their esters such as 2-hydroxy ethyl methacrylate and 2-(tertiary-butyl amino) ethyl methacrylate and their amides and nitriles), aralkenes (for example styrene) and mixtures thereof. Other monomers, such as vinyl monomers e.g. vinyl chloride, vinyl pyridine, vinyl esters (especially vinyl acetate) and vinylidene monomers, particularly the chloride may also be polymerised by our process.

Transition metal carbonyls that may be used include simple metal carbonyls containing only metal atoms and carbonyl groups including those of iron, cobalt, molybdenum, chromium, tungsten, manganese and ruthenium, for example $Mo(CO)_6$, $W(CO)_6$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, $Fe(CO)_5$, $Fe_2(CO)_{10}$, $Fe_3(CO)_{12}$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Ru_3(CO)_{12}$, and mixtures thereof.

There may also be used as the transition metal carbonyl a complex transition metal derivative having one or more other groups, not being phosphine groups, in addition to one or more carbonyl groups, attached to the metal atom; i.e. part carbonyls, for example metal carbonyl halides, metal cyclopentadienyl carbonyls and poly-metal carbonyls wherein the metal atoms are linked by bridging-ligands other than carbonyl groups, e.g. $>S.CH_3$, or $>S.C_6H_5$, as in compounds represented by the formula:—



and



Such part carbonyls are included within the term "transition metal carbonyls" throughout the specification.

The carbonyls vary in their activity and the effectiveness of each carbonyl depends upon the conditions employed; but we have found $Mn_2(CO)_{10}$ and $Fe_2(CO)_6S_2(CH_3)_2$ to be very effective, giving polymer yields of at least 80% in many cases without precautions being taken to exclude air.

For the polymerisation process, the concentration of metal carbonyl to be used is in general up to about 10^{-1} gm. mole/litre of reaction mixture. Larger proportions may be used if desired, though it may be found that little or no advantage is thereby achieved and in some cases, even, the yield may be adversely affected. It is preferred to use concentrations in the range 1×10^{-5} to 5×10^{-2} gm. mole per litre of reaction mixture.

The polymerisation may be carried out in a solvent or in the presence of a diluent or dispersion medium, or in the absence of such media, but it is particularly convenient to add the metal carbonyl as a solution.

Suitable solvents, diluents or dispersion media include ethers (for example tetrahydrofuran), esters, (for example ethyl acetate), nitriles (for example benzonitrile) and water or mixtures thereof. It should be noted, however, that not all solvents are suitable for all carbonyl compounds, but the best solvent may be readily determined in each case by simple experiment. Some solvents may act as chain transfer agents in the polymerisation process.

Where the monomer is immiscible with the diluent an emulsifier may be used to increase the area of contact between the two phases.

The halogenated organic compound for use in the process of our invention preferably contains two or more halogen ($-X$) atoms, which are either chlorine or bromine atoms, attached to the same carbon atom. It is preferred that when there are only two such halogen atoms, there should also be an electron with-drawing group ($-Y$) attached to the same atom (thus giving a compound of the structure $-CX_2Y$) otherwise it is preferred that the halogenated compound should contain the group $-CX_3$ where each X is chlorine or bromine. Examples of suitable halogenated compounds include carbon tetrachloride, chloroform, trichlorobromomethane, bromoform, carbon tetrabromide, trichlorofluoromethane, chloral, trichloroacetonitrile, benzotrichloride ($C_6H_5.CCl_3$) or mixtures thereof. Less highly halogenated compounds, for example methylene chloride and chloroacetamide, may also be used though these tend to be less effective.

Alternatively, the halogenated compound may be a polymer which contains halogen atoms in the repeating units. Thus graft polymers may be produced by the process of our invention, for example with poly(vinyl trichloracetate) or poly(vinyl monochloracetate).

As a further alternative, the halogenated compound may be a silicon-organic compound, for example a halogenated organo-silane, represented by the structure

$$m_3C-Y-SiX_3$$

where X is a halogen atom, generally chlorine or bromine and Y is a direct link or a divalent organic radical, for example a divalent hydrocarbon radical. A suitable compound of this type is a p-trichloromethyl phenyl trichlorosilane.

Silane derivatives have an affinity for glass and may be used in combination with the carbonyl and a suitable monomer for grafting polymers on to glass as disclosed in our copending British Application No. 39583/65 (Serial No. 1,138,065). The effectiveness of initiation depends to a considerable degree upon the particular components used, however, and the value of any particular halogenated compound depends upon the metal carbonyl with which it is used. The concentration of halogenated compound used is generally from 5×10^{-3} to 2×10^{-1} gm. mole/litre of reaction mixture although amounts as low as 10^{-5} gm. mole/litre may be operable in some circumstances and an upper limit is fixed mainly by reason of economy and also because of the activity of the halogen compound as a chain transfer agent.

The polymerisation may be aided by heat or by photochemical action.

The polymerisation temperatures will depend largely upon the choice of monomer. Conveniently the temperature lies in the range 20°C to 100°C, preferably 40°C to 90°C,

although higher or lower temperatures may be used if desired.

Photochemical action may be induced by ultraviolet or visible radiation. Day-light may be used, but this does not allow the degree of control possible when an artificial radiation source is used. A combination of heat and photochemical activation may also be used.

The polymerisation may be effected at substantially atmospheric pressure, although higher or lower pressures may be used if desired, particularly where the monomer is volatile. The time required for the polymerisation is dependent upon several factors, including the individual components employed, their concentration and the temperature of polymerisation.

The polymers may be isolated by conventional techniques, for example by precipitation from solution by pouring the reaction mixture into a liquid in which the polymer is sparingly soluble, for example methanol or petroleum ether. Alternatively, the polymerisation product may be dissolved in a suitable solvent (for example chloroform) and then re-precipitated by dilution with a non-solvent.

It may be convenient to isolate the polymer simply by evaporation of the unpolymerised monomer, and any solvent or diluent.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight unless otherwise stated.

Example 1

A mixture was made up containing 0.03 parts of dimanganese decacarbonyl, 0.8 parr of carbon tetrachloride and 9.5 parts of monomeric methyl methacrylate. This mixture was introduced into a polymerisation vessel which was then sealed and heated at 80°C for 2 hours. No precautions were taken to remove air. At the end of this time the tube was opened, the product dissolved in chloroform and the chloroform solution was poured into methanol to precipitate the polymer. The resulting polymer weighed 8.81 parts (92.9% yield).

Examples 2—4

In each of these examples, the procedure of Example 1 was repeated with the same quantities of carbonyl, carbon tetrachloride and monomer. The results are tabulated below:—

Example	Carbonyl	Yield	
		Parts	Per cent
2	$Mo(CO)_6$	0.21	2.2
3	$W(CO)_6$	1.11	11.7
4	$Cr(CO)_6$	0.76	8.0

For comparison, the procedure of Example 2 was repeated taking precautions to exclude air. Substantially the same yield was obtained.

A mixture was made up containing 9500 parts methyl methacrylate, 800 parts carbon tetrachloride and 10.3 parts of manganese cyclopentadienyl tricarbonyl. It was introduced into a polymerisation vessel, which was sealed and heated to 80°C. No precautions were taken to remove air. After 2 hours, 901 parts of polymer were isolated representing a yield of 9.5%.

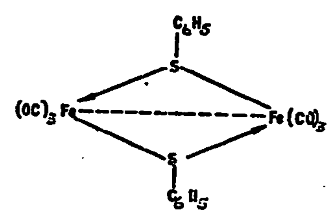
The experiment was repeated in vacuo and a yield of 12% was obtained.

Example 6

The compound of the Formula

$$Fe_2(CO)_6S_2(C_6H_5)_2,$$

which is thought to have the structure



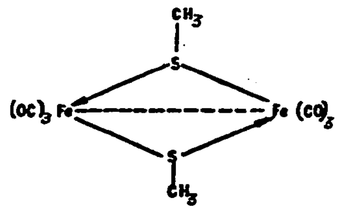
was prepared by the reaction of iron pentacarbonyl with diphenyl sulphide. When used according to the procedure of Example 1 instead of the dimanganese decacarbonyl 1.54 parts of polymer were produced representing a yield of 16.2%.

Example 7

The compound of the formula

$$Fe_2(CO)_6S_2(CH_3)_2$$

thought to have the structure



was prepared by the reaction of iron pentacarbonyl with dimethyl sulphide. When used according to the procedure of Example 1 instead of the dimanganese decacarbonyl, 7.80 parts of polymer were produced, representing a yield of 82.1%.

For comparison, the procedure of Example 7 was repeated, taking precautions to exclude air. Substantially the same yield was obtained.

EXAMPLE 8

A mixture was made up containing 9100 parts styrene, 60 parts poly(vinyl trichloracetate) (prepared by the polymerisation of vinyl trichloracetate) and 10.1 parts dimanganese decacarbonyl. The mixture was introduced into a polymerisation vessel which was then sealed and illuminated with light of 4358 Angstroms wavelength. No precautions were taken to remove air. After 9 mins. 50 secs. the reaction mixture gelled. An analogous experiment carried out in vacuum gelled in 3 mins. 45 secs. The product is believed to be a graft polymer of poly(styrene)onto poly (vinyl trichloracetate).

EXAMPLE 9

A mixture was made up containing 1 part dimanganese decacarbonyl, 79 parts carbon tetrachloride and 940 parts methyl methacrylate. This mixture was introduced into a polymerisation vessel which was then sealed and irradiated with light of 4358 Angstroms wavelength for 2 hrs. No precautions were taken to remove air. At the end of this time the tube was opened and the product dissolved in chloroform. The resultant solution was poured into methanol to precipitate the polymer, which was obtained in 94.5% yield. An analogous experiment carried out in vacuum gave a yield of 94.9%.

EXAMPLE 10

A mixture was made up containing 10.7 parts dimanganese decacarbonyl, 41.5 parts poly(vinyl trichloracetate), (prepared by the trichloroacetylation of polyvinyl alcohol) and 11000 parts 2-(tertiary butyl amino)ethyl methacrylate. This mixture was introduced into a polymerisation vessel which was then sealed and irradiated with light of 4358 Angstroms wavelength. No precautions were taken to remove air. The reaction mixture gelled in 28 mins. The product is believed to be a graft polymer of poly[2-(tertiary-butylamino) ethyl methacrylate] onto poly(vinyl trichloracetate).

EXAMPLE 11

A reaction mixture was made up containing 17200 parts vinyl perfluorobutyrate, 10.4 parts dimanganese decacarbonyl, and 240 parts carbon tetrachloride. This mixture was introduced into a polymerisation vessel which was then sealed and heated at 80°C. for 24 hrs. No precaution was taken to remove air. At the end of this time the product was isolated by evaporating off the unchanged monomer giving a yield of polymer of 40.3%.

EXAMPLE 12

A reaction mixture was made up containing 1000 parts methacrylic acid, 15 parts p-trichloromethylphenyl trichlorosilane and 1 part dimanganese decacarbonyl. This mixture was introduced into a polymerisation vessel which was then sealed and heated at 80° for 2 hrs. No precautions were taken to remove air. At the end of this time the product was isolated by evaporating off the unchanged monomer giving a yield of 13.0%

EXAMPLE 13

A reaction mixture was made up containing 910 parts styrene, 1 part dimanganese decacarbonyl and 15 parts p-trichloromethylphenyl trichlorosilane. This mixture was introduced into a polymerisation vessel which was then sealed and heated at 80° for 2 hrs. No precautions were taken to remove air. At the end of this time the tube was opened, the product was dissolved in chloroform and the chloroform solution poured into methanol to precipitate the polymer. The yield was 45.2%.

EXAMPLE 14

A mixture was made up containing 9500 parts of methylmethacrylate, 790 parts of carbon tetrachloride and 28.7 parts of dicobalt octacarbonyl. This mixture was introduced into a polymerisation vessel which was then sealed and heated at 80° for 2 hrs. No precautions were taken to remove air. At the end of this time the tube was opened the product dissolved in chloroform and the chloroform solution was poured into methanol to precipitate the polymer. The resulting yield of polymer was 56.2%. An identical experiment carried out in high vacuum gave a yield of 57.8%.

EXAMPLE 15

5.3 parts triruthenium dodecacarbonyl, 790 parts CCl_4 and 9400 parts distilled methyl methacrylate were placed in a reaction tube and shaken to dissolve the $Ru_3(CO)_{12}$. After bubbling air through the mixture for several minutes the tube was sealed and placed in a

water bath at 80°C for 30 minutes. The tube was then opened and the contents plus chloroform washings were poured into methanol to precipitate the polymethyl methacrylate formed. The polymer was filtered, purified by dissolving in chloroform and reprecipitating in methanol, filtered off again and dried in a vacuum oven at 40°C. The yield of polymethyl methacrylate was 9.8%.

EXAMPLE 16

The procedure of Example 15 was repeated using 5.4 parts $Ru_3(CO)_{12}$ and reacting for 1 hour at 80°C. The yield of polymethyl methacrylate was 20.8%.

EXAMPLES 17—21

To investigate the effect of varying the solvent, reaction mixtures were prepared using approximately 1 part dimanganese decacarbonyl, 320 parts methyl methacrylate, 24 parts carbon tetrachloride and the amount of the selected solvent shown in the Table. In the case of water, an emulsion was prepared using 10 parts sodium dodecyl benzene sulphonate per 60 parts water.

The mixture was introduced into a polymerisation vessel which was sealed and heated at 80°C for 2 hrs. No precautions were taken at any stage to remove air. At the end of this time the polymer was isolated by pouring the product mixture into methanol, filtering and drying.

Results are shown in the Table below:—

Example	Solvent	Amount (parts)	% Yield of Polymer
17	Water	680	84.6
18	Toluene	590	31.1
19	Ethyl Acetate	620	33.0
20	Tetrahydrofuran	600	74.2
21	Benzonitrile	685	43.7

EXAMPLES 22 AND 23

The procedure of Examples 17—21 was repeated varying the halide source. No solvent was added but the amount of methyl methacrylate used was increased to 950 parts. The amount of halide used is shown in the Table:—

Example	Halide	Amount (parts)	% Yield of Polymer
22	Benzo-trichloride	20	91.4
23	Chloroform	22	64.8

EXAMPLES 24—27

The procedure of Examples 17—21 was repeated, varying the monomer but without solvent. The amount of monomer was as shown in the Table. 24 parts carbon tetrachloride were used.

Example	Monomer	Amount (parts)	% Yield of Polymer
24	Vinyl pyridine	1077	84.7
25	Methacrylic acid	950	91.7
26	2-Hydroxyethyl methacrylate	1085	40.3
27	2(Tert-butylamino)ethyl methacrylate	1110	40.8

WHAT WE CLAIM IS:—

1. A process for polymerising ethylenically unsaturated material normally polymerisable by a free radical mechanism which comprises contacting the material with a transition metal carbonyl in the presence of a halogenated organic compound and in the presence of more than 100 parts per million by volume of atmospheric oxygen.

2. A process for polymerising ethylenically unsaturated material normally polymerisable by a free radical mechanism which comprises contacting the material with a transition metal carbonyl in the presence of a halogenated organic compound without any precautions being taken to remove atmospheric oxygen.

3. A process as claimed in claim 1 or claim 2 in which the ethylenically unsaturated material contains an electron-attracting group.

4. A process as claimed in claim 3 in which the ethylenically unsaturated material is acrylic acid, a substituted acrylic acid or a functional derivative thereof.

5. A process as claimed in claim 3 in which the ethylenically unsaturated material is a vinyl or vinylidene monomer.

6. A process as claimed in claim 3 in which the ethylenically unsaturated material is an aralkene.

7. A process as claimed in any one of claims 1—6 in which the transition metal carbonyl is a simple metal carbonyl containing only metal atoms and carbonyl groups.

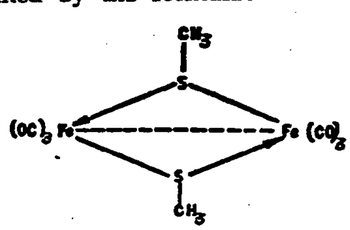
8. A process as claimed in claim 7, in which the transition metal carbonyl is a carbonyl of iron, cobalt, molybdenum, chromium, tungsten, manganese or ruthenium or a mixture of any of these.

9. A process as claimed in claim 8 in which the transition metal carbonyl is dimanganese decacarbonyl.

10. A process as claimed in any one of claims 1—6 in which the transition metal carbonyl is a complex carbonyl containing one or more other groups, not being phosphine groups, in addition to one or more carbonyl groups attached to the metal atom.

11. A process as claimed in claim 10 in which the complex carbonyl contains two or more metal atoms, which are linked by bridging groups other than carbonyl or phosphine groups.

12. A process as claimed in claim 11 in which the complex carbonyl is the compound represented by the formula:—



13. A process as claimed in any one of claims 1—12 in which the concentration of transition metal carbonyl is from 1×10^{-5} to 1×10^{-1} gm. mole per litre of reaction mixture.

14. A process as claimed in claim 13 in which the concentration of transition metal carbonyl is from 1×10^{-5} to 5×10^{-2} gm. mole per litre of reaction mixture.

15. A process as claimed in any one of claims 1—14 in which the reaction is carried out in the presence of a solvent, diluent or dispersion medium.

16. A process as claimed in any one of claims 1—15 in which the halogenated organic compound contains two or more chlorine or bromine atoms attached to the same carbon atom.

17. A process as claimed in claim 16 in which the halogenated organic compound contains an electron-withdrawing group attached to the same carbon atom as the halide atoms.

18. A process as claimed in claim 16 or claim 17 in which the halogenated organic compound contains the group $—CX_3$ where X is chlorine or bromine.

19. A process as claimed in claim 16 in which the halogenated organic compound is carbon tetrachloride.

20. A process as claimed in any one of claims 1—18 in which the halogenated organic compound is a polymer containing halogen atoms in the repeating units.

21. A process as claimed in claim 20 in which the halogen-containing polymer is poly-(vinyl trichloracetate) or poly-(vinyl monochloroacetate).

22. A process as claimed in any one of claims 1—15 in which the halogenated organic compound is a halogenated organo-silane.

23. A process as claimed in claim 22 in which the organo-silane is a chloro- or bromo-silane.

24. A process as claimed in claim 23 in which the organo-silane is p-trichloromethyl-phenyl trichlorosilane.

25. A process as claimed in any one of the preceding claims in which the concentration of halogenated organic compound in the reaction mixture is in the range 10^{-5} to 2×10^{-1} gm. mole per litre.

26. A process as claimed in claim 25 in which the concentration of halogenated organic compound in the reaction mixture is in the range 5×10^{-3} to 2×10^{-1} gm. mole per litre.

27. A process as claimed in any one of the preceding claims in which the polymerisation is carried out in the temperature range 20—100°C.

28. A process as claimed in claim 27 in which the polymerisation is carried out in the temperature range 40—90°C.

29. A process as claimed in any one of

claims 1—28 in which the polymerisation is carried out under the influence of ultraviolet or visible radiation.

30. A process as claimed in any one of claims 1—29 in which the reaction is carried out at substantially atmospheric pressure.

31. A process for polymerising ethylenically unsaturated material normally polymerisable by a free radical mechanism according to claim 1 or claim 2 substantially as described in any one of the Examples.

32. A polymer whenever produced by a process as claimed in any of the preceding claims.

D. PRICE,
Agent for the Applicants.

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